Source and occurrence of particulate lead in tap water

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article info

abstract

Lead samples were collected at the tap from homes with lead service lines (LSLs) in a full-scale utility using both random daytime (RDT) and particulate stimulation sampling (PSS) protocols. Analysis of the results revealed two sources and occurrences of particulate lead. A first source is due to corrosion of lead-bearing elements in the premise plumbing (PP) and occurs mostly at low to moderate concentrations <3mg/L, with some sporadic higher concentrations (4e12mg/L). These spikes were consistently observed and considerably increased using PSS, showing that current sampling protocols may miss a significant portion of particulate lead. The second source results from the adsorption of dissolved lead onto iron deposits in LSL/PP, and is continuously present at low to moderate concentrations. Statistical analyses were validated by physical analyses of: (i) lead scales from LSLs; and (ii) lead particles from tap aerators.

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1. Introduction

Lead in drinking water is a major public health concern. It can create irreversible intellectual impairment in infants and young children, even at blood lead levels (BLLs) below 10mg/dL (Lanphear et al., 2000; Gump et al., 2008; Jusko et al., 2008). Assessing the impact of lead from tap water on BLLs can be difficult due to multiple exposure pathways, temporal variability of waterborne lead, and inter-individual and day-to-day variability in exposure studies (Schock, 1990; Lanphear et al., 2002). Nonetheless, the rise in lead levels in tap water significantly increased the number of children with elevated BLLs in some studies (Lanphear et al., 1998; Edwards et al., 2009). Lanphear et al. (2002) also reported that water lead levels above 5mg/L after 1min of flushing significantly increase the BLLs of children aged 6e24 months. Finally, recent cases of lead intoxication in children have been related to solder particle ingestion (Triantafyllidou et al., 2007).

Numerous utilities still serve homes with lead service lines (LSLs), which can contribute to 50e75% of the total lead mass measured at the tap during profile sampling and for which a replacement time frame is a commitment issue (Sandvig et al., 2008). Lead in tap water is also increased by leaching from lead-bearing materials in premise plumbing (PP), such as lead-tin solders containing up to 50% lead (Subramanian et al., 1995), and brass materials containing up to 8% lead (Dudi et al., 2005).

Current standards and guidelines on lead in drinking water are mostly in the 0.010e0.015 mg/L range; however, sampling protocols differ widely among countries, in terms of variations

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in stagnation time, sampling volume, and number of samples collected, which influence the recovery of lead (Schock, 1990). The US action level is set at 0.015 mg/L in at least 90% of the samples collected from high-risk locations. The sampling protocol consists of taking a 1L sample of cold tap water after at least 6 h of stagnation, and aims to assess the contribution of both LSL and PP. However this approach can underestimate peak concentrations occurring in subsequent liters, depending on PP volume (Giani et al., 2005). In Europe, random daytime (RDT) sampling (1st liter taken during office hours, without fixed stagnation) and sampling after 30 min of stagnation (30MS) (1st and 2nd liter) were identified as the best approaches for estimating exposure and detecting homes with elevated lead concentrations in tap water. RDT is cost-effective and convenient for consumers, when compared to 30MS sampling; however, it is difficult to reproduce (van den Hoven and Slaats, 2006). Health Canada recently issued a corrosion control guidance document (Health Canada, 2009) combining both the American and the European approaches: 1st option is performed following the LCR protocol, and 2nd option is based on 30MS sampling. Compliance in Ontario (Canada) is based on meeting a 0.010 mg/L action level in the highest of the two subsequent liters taken after 30MS in at least 90% of homes sampled (Government of Ontario, 2002).

Particulate lead is usually defined as the fraction of lead retained by a 0.45mm filter. Current sampling protocols and methods of analysis may underestimate total lead because of particulate lead. The prescribed EPA 200.8 method recommends digesting samples directly in the bottle with nitric acid at pH < 2 for at least 16 h at 4°C, and then, if turbidity exceeds 1 NTU, performing a rigorous heated-digestion on an aliquot of the sample. However, this method may not entirely dissolve lead solders and lead (IV) oxide particles, which may underestimate particulate lead (Triantafyllidou et al., 2007). Also, if samples are not acidified immediately, low soluble tetravalent lead particles can adhere to the sampling bottles, resulting in a turbidity reading below 1 NTU, and consequently to total lead underestimation (Edwards and Dudi, 2004). Furthermore, particulate lead losses can occur when the aliquot is extracted for the heated-digestion, and when the hot-digested aliquot is centrifuged prior to analysis. Finally, suspended colloidal lead in the centrifuged vial may not be quantified by the usual analytical methods (Triantafyllidou et al., 2007).

Sampling approaches prescribed by regulation do not include the filtration of samples, therefore, could estimate total lead. However, the prescribed conditions are designed to prevent the adsorption of dissolved lead onto the bottle and its precipitation, not the optimal solubilization of particulate lead. Dissolved lead increases with stagnation time until it reaches the equilibrium level (within 8e24 h) and its source can be estimated by measuring concentration profiles, PP and LSL length. In contrast, particulate lead occurs sporadically and is mainly caused by physical factors, making its contribution difficult to predict with any certainty (Schock, 1990; Triantafyllidou and Edwards, 2009). The transport of particles that detach from LSL/PP to the tap depends on flow rate, hydraulic regimen, and particle characteristics (Slaats et al., 2003). Particulate lead occurrence increases with increasing flow rate; though, protocols specify sampling at a low flow

rate, lower than typical faucet usage (w7e12 L/min) (Triantafyllidou and Edwards, 2009).

Thus, existing sampling protocols and analytical methods were not developed to detect particulate lead, and so may underestimate total lead exposure. The main objectives of this study were: (i) to characterize the source and occurrence of particulate lead in homes supplied with water by LSLs; and (ii) to evaluate a protocol method to detect particulate lead specifically.

2. Materials and methods

2.1. Distribution system: general characteristics and water quality

The 45 homes sampled were selected on the basis that they represent all the communities served by the distribution system and the presence of lead in at least a part of the service line (6 partial LSLs). Two types of homes were sampled: "wartime", built during WWII, with 2e3 times longer LSLs than those built "before 1970", as observed during sampling. Inside piping in all homes was mainly made of copper, except in 3 cases (either galvanized-iron (n¼1) or a mix of lead and copper pipes with the majority being copper (n¼2)). Table 1 summarizes the water quality parameters of the system studied, and information on the configuration and sampling parameters of the homes studied.

2.2. General protocol

30MS sampling is defined as sampling after 30 min of stagnation preceded by 5 min of flushing, and the collection of the 1st liter, 2nd liter, one liter after 1 min of flushing, and one liter after 5 min of flushing. RDT sampling is defined as the immediate sampling after entering the home without fixed stagnation or any flushing (1st liter: 1 L; 2nd liter: 2 L; liter after 5 min:5 min). Samples were collected in cold water (kitchen tap) at "normal" flow rate (typically ⌐ 8 L/min).

Between May and July 2006, 109 "wartime" and "before 1970" homes were sampled using a 30MS protocol, this protocol was not the goal of the study (RDT-2007), but will serve as a basis for comparison in the discussion. Between July and September 2007, 45 homes were sampled using RDT. Among these homes, 23 were sampled in 2006 and others were in the same range of age and configuration (Table 1). Between the 2nd liter and the liter after 5 min, physico-chemical parameters potentially affecting lead leaching were measured: flow rate, temperature (mercury thermometer, SM 2550-B), pH (Oakton PhTestr 10, SM4500-H^{b} B), and free, total and combined chlorine (Hach Pocket Colorimeter II, 4500-CL G). Dissolved metals were obtained by on-site filtration immediately after the 1 L sample collection using the following procedure: each bottle was mixed, then a 50 mL aliquot was taken using a 60 mL disposable syringe (BD Luer Lok⌐), and filtered in a 50 mL vial using a 0.45mm porosity PVDF membrane cartridge (Millipore Millex HV, Durapore, 33 mm). In addition, experiments with standard multi-metal solutions at two different concentrations (5 and 10mg/L) showed that these filters do not absorb significant levels of the

Table 1 e Water quality characteristics of the system studied and information on the configuration and sampling parameters of the homes sampled.

Annual water quality characteristics of the system studied		Configuration and sampling parameters of homes sampled in 2007 (range/mean)			
pH	7.47e8.15	pH	7.5e7.8 Mean: 7.65	LSL length (m)	6.0e30.2 Mean: 14.6
Turbidity (NTU)	0.09e1.63	Turbidity (NTU)	0.09-0.9 Mean: 0.16	"Wartime" LSL length (m)	15.4e30.2 Mean: 22.0
Temperature ($^{\circ}$C)	1.5e25.5	Temperature ($^{\circ}$C)	18.3e22.8 Mean: 21.3	"Before 1970" LSL length (m)	6.0e20.7 Mean:11.9
Alkalinity (mgCaCO$_3$/L)	78e86				
DIC (mg/L)	120	Free chlorine (mg/L)	0.0e1.1 Mean: 0.53	PP length(m)[a]	1.0e38.0
Total hardness (mgCaCO$_3$/L)	111e121			LSL diameter (cm)[a]	1.27e2.54
Conductivity (mS/cm)	275e307	Flow rate (L/min)	1.0e12	Volume of LSL (L)[a]	0.33e5.98
Total solids (mg/L)	160e188		Mean: 5.7	Volume of PP (L)[a]	0.13e6.46

a Data from 2006 sampling.

metal tested (difference $<^{\lrcorner}$ 0.05 mg Pb/L, $<^{\lrcorner}$ 0.06 mg/L for other metals) but could release dissolved zinc (up to 13 mg/L). Samples were transported to the laboratory and acidified preferentially the day of the sampling or within 24 h (precisions 2.4). LSLs were sampled (scraping), and LSL lengths were measured on-site. After water sampling, particles retained by the tap aerator were collected and excess water was removed to avoid particle oxidation.

2.3. Particulate stimulation sampling (PSS)

In 2007, additional PSS was added after RDT sampling in 9 homes, in order to stimulate particulate lead detachment. Following the collection of the last RDT sample (5 min), a 1 L bottle (S1) was placed under the closed tap, and then the tap was opened and closed 5 times at maximal flow rate. The bottle was then completely filled at normal flow rate. The 2nd liter, S2, was collected immediately after, S1, at normal flow rate. The 3rd liter, S3, was collected using the same procedure as described for S1.

2.4. Laboratory analysis

Lead, copper, iron, zinc, cadmium, and antimony were measured for dissolved and particulate forms using an ICP-MS (Agilent 7500a). In 2007, tin was also analyzed (ICP-MS Agilent 7500cs). The particulate metal fraction was determined by deducting total metal from dissolved metal. ICP-MS detection limits (mg/L) were: Cd ¼ 0.03; Cu ¼ 0.09; Fe ¼ 5; Pb ¼ 0.02; Sb ¼ 0.03; Sn ¼ 0.1; Zn ¼ 0.4. For low concentrations of total zinc, the release of soluble zinc from the filter led to some negative values of particulate zinc. Because of the very high positive values of particulate zinc when present (up to 632 mg/L), negative values were kept and assigned a zero value. Polypropylene sampling bottles and vials were washed using the following procedure (System Plus Ltd, method C): phosphate-free detergent wash, nitric acid rinse, ultra-pure water rinse, and drying in a lead-free environment. Samples were acidified at pH < 2 by adding 0.5% HNO$_3$ (optima grade, Fisher Scientific), and stored for at least 16 h at 4 $^{\circ}$C before analysis. If turbidity in the 1st liter exceeded 1 NTU, samples underwent a heated-acid digestion: 0.5% HCl þ 0.5% HNO$_3$, 2 h, 95 $^{\circ}$C (ICP-MS manufacturer's recommendations). Preliminary testing investigating the impact of heated-acid digestion was

performed on 76 samples in 2006 (19 samples of each type: 1 L, 2 L, 1 min, 5 min). Every sample underwent digestion, using the EPA 200.8 protocol (16 h, 4 $^{\circ}$C, pH < 2), and was analyzed for lead, followed by further digestion at 85 $^{\circ}$C f or 48 h (pH < 2) and analyzed for lead again. Lead concentrations measured by the two digestion methods did not vary significantly and t-tests comparing the two values were not significant(p > 1). Thus, the EPA 200.8 digestion standard was used for all samples.

On-site and laboratory measurements were analyzed using Statistica statistics software (version 8.0, StatSoft). Significant factors were stated for p < 0.05.

2.5. LSL deposits and particles analysis

Six LSLs were collected between July and October 2007 from three districts well spaced out on the distribution system (two per district). Pipes were handled horizontally after plugging each opening to keep the humidity inside the pipes. Interior scale was studied on multiple spots using micro-RAMAN inVia spectroscopy and ION TOF-SIMS IV. The RAMAN analysis conditions were: wavelength 785 nm, power 5e10%, magnifying power 20| or 50| , acquisition time w 50 s, and spectrum width 200e2000 cm$^{\lrcorner 1}$. These conditions were adjusted using preliminary testing because the power of the laser beam and the time of exposure could denature the sample. Selected standards (Alfa-Aesar) included: Pb (99% (metal basis)), PbO (99%), PbO$_2$ (Lead IV oxide, 97%), PbCO$_3$ (PbCO$_3$ ACS grade), (PbCO$_3$)$_2$Pb(OH)$_2$ (basic, 99% (metal basis)), and Pb$_3$O$_4$ (Lead (II, IV) oxide). TOF-SIMS analysis conditions were: ^{69}Ga[b] ion source, 25 keV energy, static mode, 3.7 pA current, acquisition surface 20 | 20 mm, and mass resolution on ^{29}Si – 8000. Charge neutralization was achieved with an electron flood gun.

Ten typical particles taken from tap aerators (2007) were analyzed by TOF-SIMS. Conditions were the same as for LSL analysis, except for current (2.7 pA), mass resolution on ^{29}Si (– 9000), and acquisition zone (40 | 40 mm and 9 | 9 mm).

3. Results

3.1. Sampling

Fig. 1(a,b) presents dissolved and particulate lead concentrations versus sample type for 2007 RDT sampling. All sample

types were considered on a 90th percentile basis, dissolved lead and particulate lead representing 94e96% and 4e6% of total lead respectively. Dissolved lead levels were comparable for the 1st and 2nd liters (90th percentile: 43 and 44 mg/L, respectively), and drop twofold and significantly after 5 min of flushing (p < 0.05, Kruskal-Wallis test). The particulate lead profile differed because concentrations decreased after the 1st liter (2L-RDT) but not significantly so with the liter collected after 5 min flushing (p < 0.01, Kruskal-Wallis test).

Fig. 2 illustrates the cumulative distribution of particulate lead for each type of RDT sample. The 90th percentile in the 1st liter was half the WHO guideline value of 0.010 mg/L, and maximum values were higher than this value. For the 2nd liter and the liter after 5 min, the 90th percentile and median decreased rapidly. However, some higher values (2 L: 4.5e7.4 mg/L; 5 min: 2.5e3.5 mg/L) remaining after flushing the 1st liter showed that partial rinsing was insufficient to avoid the sporadic occurrence of particulate lead.

Table 2 presents metal levels measured in tap water for RDT and PSS samplings (2007). Cadmium and antimony were not considered further in the analysis, either because their levels were constant (Sb) or below detection limits (Cd).
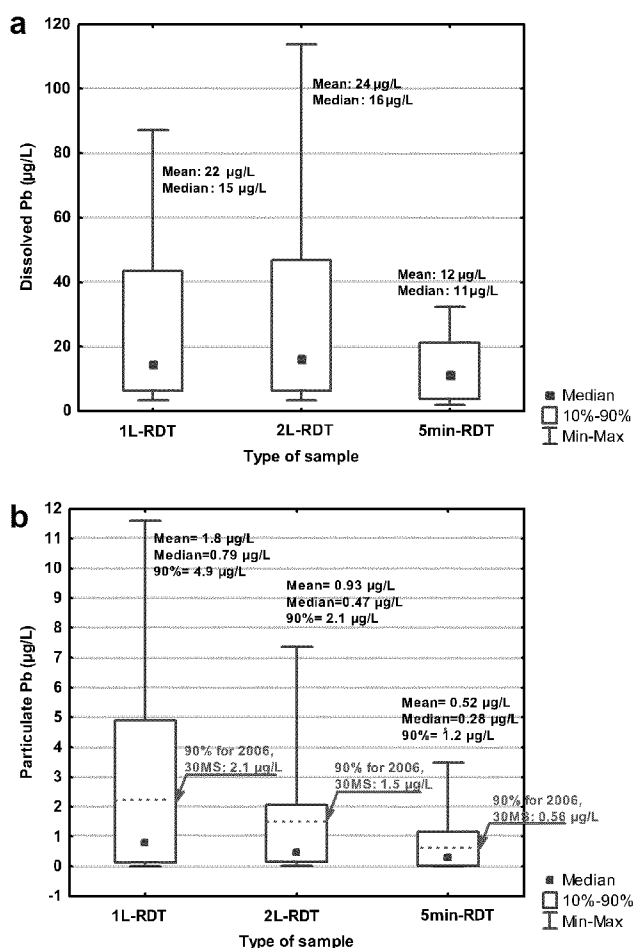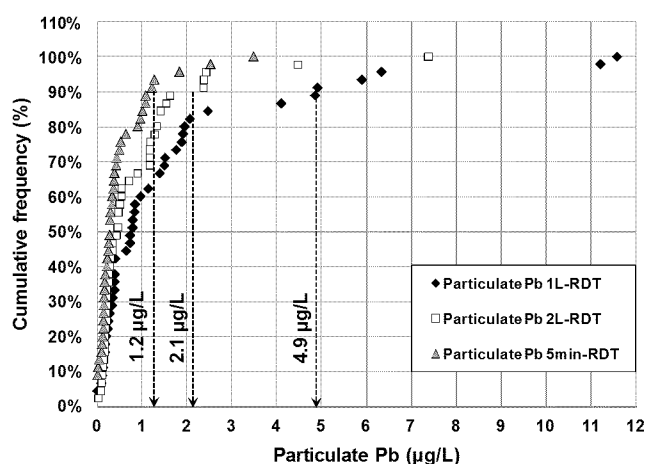

Fig. 2 e Cumulative frequency (%) vs. particulate Pb concentration (mg/L) for each type of sample, RDT sampling 2007.

3.2. Statistical analyses

Table 3 introduces correlations between dissolved lead, particulate lead, and other metals. For RDT samples, dissolved lead in the 1st and 2nd liters was not correlated with any of the other metals. On the contrary, particulate lead in the 1st liter was clearly correlated with metals from PP and iron (p < 0.01): particulate zinc (R¼0.61), dissolved iron (R¼0.47), particulate iron (R¼0.58), particulate tin (R¼0.44), and particulate copper (R¼0.43). Most of the time, high particulate zinc values and particulate lead spikes occurred simultaneously. In the 2nd liter and the liter after 5 min, particulate lead correlation with particulate iron (R¼0.83e0.88, p < 0.01) and dissolved iron increased (R¼0.70e0.76, p < 0.01), while correlations with PP metals nearly disappeared (particulate Cu only). Also, after 5 min of flushing, dissolved lead and particulate lead were significantly correlated (R¼0.32, p < 0.04), suggesting a common source.

Multiple regression analyses were performed on particulate lead versus metals in water, and sampling parameters potentially affecting particulate lead release (flow rate, pH, chlorine, turbidity, temperature, LSL length). Data were separated by sample type for a two-step analysis (1 L, 2 L, 5 min): (i) particulate lead versus other metals, (ii) particulate lead versus sampling parameters. Temperature, pH and chlorine did not significantly affect lead release. The length of LSL, even if well distributed (6.0e30 m) and correlated with dissolved lead (Cartier et al., 2008), was not correlated with particulate lead. Moreover, t-tests showed that particulate lead was not significantly different in homes "before 1970" and "wartime" (p > 0.2 for 1L-RDT, 2L-RDT, 5min-RDT) even if the latter had significantly longer LSLs. Factors significantly associated with particulate lead in the 1st liter included turbidity ($R^2_{adjusted}$ ¼0.48, p < 0.01), particulate iron, particulate zinc, and dissolved lead ($R^2_{adjusted}$ ¼0.64, p < 0.01). Particulate tin was almost significant (p ¼0.07), and all metals increased with particulate lead (Fig. 3a). The data also revealed that particulate lead spikes and particulate spikes of zinc, tin, iron, or copper, or a combination of these metals, occurred simultaneously.

Fig. 1 e Dissolved Pb (a) and particulate Pb (b) concentrations versus type of sample in 2007 RDT sampling. N [45 homes for each box.

Table 2 e Concentrations of metals analyzed at the tap (mg/L), 2007.

Metals	RDT sampling 2007: 1 L, 2 L, 5 min						PSS sampling 2007: S1, S2, S3					
	N	Average	Median	Min	Max	90th	N	Average	Median	Min	Max	90th
Pb_{diss}	135	19	14	2.1	114	43	27	23	16	3.8	69	56
Pb_{part}	135	1.1	0.39	BDL	12	2.4	27	8.2	2.9	0.36	50	27
Cu_{diss}	135	176	96	9.4	780	440	27	143	141	33	332	227
Cu_{part}	135	3.4	1.2	BDL	47	9.0	27	16	9.5	BDL	175	25
Fe_{diss}	135	22	16	BDL	130	58	27	23	17	BDL	71	69
Fe_{part}	135	10	3.2	BDL	247	17	27	9.1	4.8	BDL	48	36
Zn_{diss}	135	22	11	3.5	220	37	27	14	13	6.3	41	22
Zn_{part}	135	1.1	e	BDL	119	e	27	58	6.0	BDL	632	327
Sn_{diss}	135	e	e	BDL	0.23	e	27	0.01	e	BDL	0.18	e
Sn_{part}	135	0.03	BDL	BDL	1.3	0.02	27	2.5	0.44	BDL	33	4.5
Cd_{diss}	135	e	e	BDL	0.03	e	27	e	e	BDL	e	e
Cd_{part}	135	e	e	BDL	BDL	e	27	e	e	BDL	0.04	e
Sb_{diss}	135	0.16	0.16	0.13	0.23	0.18	27	0.15	0.15	0.13	0.17	0.17
Sb_{part}	135	e	e	BDL	0.06	0.02	27	e	e	BDL	0.02	0.02

Note: BDL means below detection limit.

Flow rate was significantly correlated with particulate lead in the 2nd liter ($R^2_{adjusted}$ ¼ 0.12, p < 0.02), as did particulate and dissolved iron, total zinc, and dissolved lead ($R^2_{adjusted}$ ¼ 0.86, p < 0.01) (Fig. 3b). After 5 min of flushing (Fig. 3c), the same factors were significant for particulate lead in the 2nd liter, except for total zinc.

Linear regressions showed a stronger relationship between particulate lead and particulate iron than with dissolved iron (Table 4). The lower level of association with dissolved iron is readily understandable considering the low solubility of ferric oxyhydroxides at pH 7.5e7.8. For the 2L-RDT and the 5min-RDT analysis on particulate lead versus particulate iron, few values (n ¼ 2 for 2L-RDT, n ¼ 3 for 5min-RDT) were outside the prediction interval (0.95). Interestingly, four of these outliers corresponded to the highest flow rates measured (8.7 and 12 L/min).

3.3. Particulate stimulation sampling (PSS)

Fig. 4 presents RDT and PSS results on particulate lead for the 9 homes. RDT results show that flushing decreased particulate lead when sampling flow rates were used (2.1e8.7 L/min). Tap stimulation (S1) dramatically increased the levels of particulate lead, far more than the levels found in 1 L-RDT (90th percentile þ 16 mg/L). Levels decreased somewhat in sample S2 without any added faucet operation. Finally, the 2nd tap stimulation (S3) created another remarkable increase in particulate lead, with the 90th percentile value more than double that observed for S2 (29 mg/L versus 12 mg/L). The 90th percentile value for S3 was also higher than that measured for S1, however, the maximum values were lower (33 mg/L versus 50 mg/L). Considering the limited number of homes investigated with PSS, the establishment of significant correlations with other metals was not possible. Particulate metals from PP also increased with PSS (Table 2, Fig. 5b): the 90th percentile values measured for S1, S2, and S3 taken together are: 4.5 mg Sn_{part}/L, 25 mg Cu_{part}/L, and 327 mg Zn_{part}/L. Particulate iron also increased, but not as much. Also, although no stagnation was provided prior PSS, notable increases in the concentrations of dissolved lead (mean þ 8.3 mg/L), zinc (mean þ 6.7 mg/L), and copper (mean þ 88 mg/L) are measured for PSS when compared to the values after 5 min RDT flushing (Fig. 5a). Iron concentrations remained stable (mean þ 1 mg/L only).

Table 3 e Correlations (R) between metals analyzed at the tap, 2007 RDT sampling.

Variable	Pb_{diss}1 L	Pb_{part}1 L	Variable	Pb_{diss}2 L	Pb_{part}2 L	Variable	Pb_{diss}5 min	Pb_{part}5 min
Pb_{diss}1L	1.0	0.14	Pb_{diss}2L	1.0	0.15	Pb_{diss}5min	1.0	0.32
Pb_{part}1L	0.14	1.0	Pb_{part}2L	0.15	1.0	Pb_{part}5min	0.32	1.0
Cu_{diss}1L	⌐0.01	⌐0.12	Cu_{diss}2L	⌐0.23	⌐0.19	Cu_{diss}5min	⌐0.28	⌐0.16
Cu_{part}1L	0.04	0.43	Cu_{part}2L	⌐0.07	0.22	Cu_{part}5min	⌐0.13	0.59
Fe_{diss}1L	⌐0.06	0.47	Fe_{diss}2L	⌐0.04	0.70	Fe_{diss}5min	0.08	0.76
Fe_{part}1L	⌐0.19	0.58	Fe_{part}2L	⌐0.05	0.88	Fe_{part}5min	⌐0.04	0.83
Zn_{diss}1L	⌐0.06	0.14	Zn_{diss}2L	⌐0.24	⌐0.09	Zn_{diss}5min	⌐0.27	⌐0.09
Zn_{part}1L	0.05	0.61	Zn_{part}2L	N.D.	N.D.	Zn_{part}5min	N.D.	N.D.
Sn_{diss}1L	0.17	0.03	Sn_{diss}2L	N.D.	N.D.	Sn_{diss}5min	N.D.	N.D.
Sn_{part}1L	0.09	0.44	Sn_{part}2L	0.05	0.00	Sn_{part}5min	N.D.	N.D.

Note: ND means not defined.
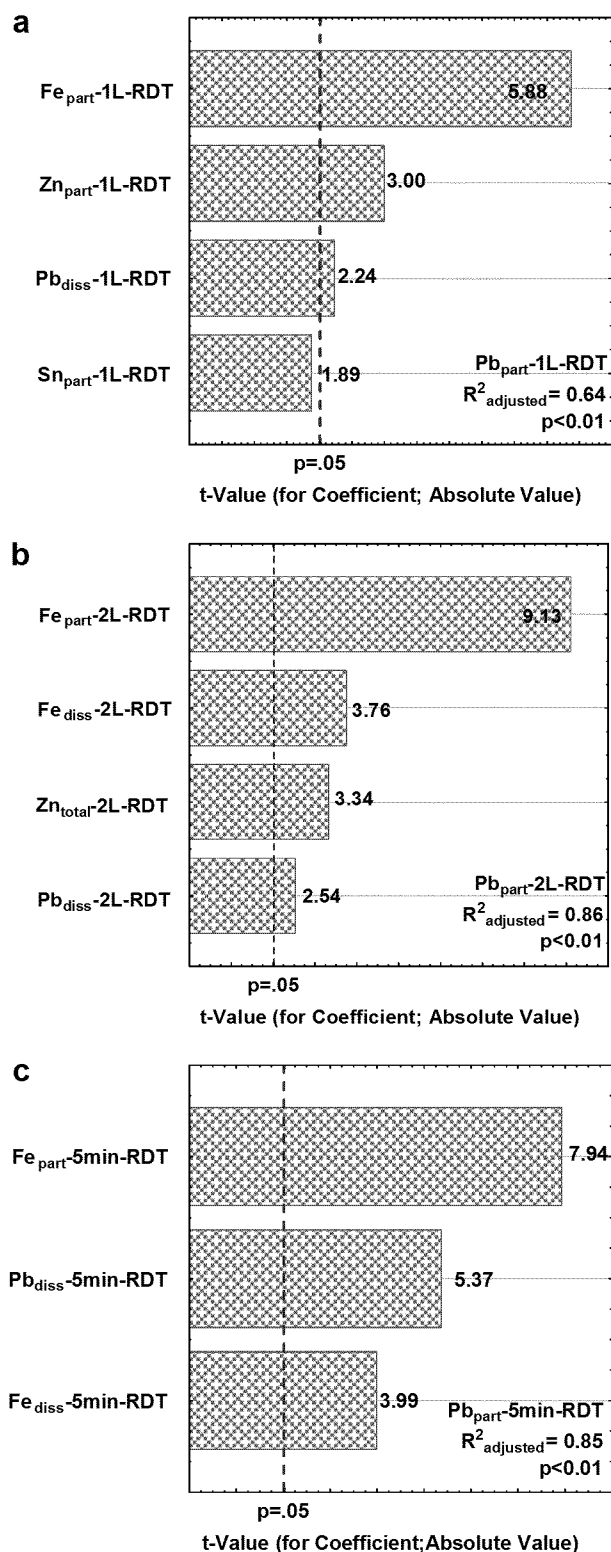Significant correlations (p < 0.05) are in italic font.

a

b

c

Fig. 3 e Multiple regressions on particulate Pb 2007 results, 45 homes, inputs [metals measured at the tap. (a) Particulate Pb 1L-RDT, (b) Particulate Pb 2 L-RDT, (c) Particulate Pb 5 min-RDT.

3.4. Scale deposits and particles

Micro-RAMAN spectroscopy carried out on two LSLs from the first district (A, B) showed six characteristic peaks of both cerussite ($PbCO_3$) and hydrocerussite (($PbCO_3$)$_2Pb(OH)_2$), including the main peak at 1055 cm^{-1}. A peak at 1386 cm^{-1} specific to cerussite was noted, as well as, two peaks characteristic of massicot/litharge (PbO), including the main peak (290 cm^{-1}). Thus, these two species were both present. Some peaks specific to tetravalent lead (PbO_2) were possibly present, but, because of their weak intensity, along with noise interference, and the absence of a main peak (510 cm^{-1}), this could not be confirmed. Also, due to the limitations in intensity and exposure time explained previously, there was little possibility of spectrum improvement. Regarding the second district (C, D), PbO peaks (343 cm^{-1}, 427 cm^{-1}) were noted on most spectra acquired, but the main peak at 290 cm^{-1} was not measured. Cerussite and hydrocerussite peaks detected were superposed, impeding differentiation of both species. Some peaks of weak intensity could be attributed to PbO_2, with strong reservation, because of noise interference and absence of the main characteristic peak. In the last municipality, the two LSLs (E, F) came from adjacent homes, but, surprisingly, one presented whitish scale (E) and the other reddish scale (F) (Photo 1a). However, despite being careful during the transportation of the pipes, it is possible that some scales could have become dislodged during the extraction, explaining the color difference. Whitish scale analysis revealed the presence of cerussite and/or hydrocerussite (peaks superposed) and PbO. Three peaks for PbO_2 were recurrent and marked: 387, 600, and 607 cm^{-1}. Thus, even in the absence of the main PbO_2 characteristic peak, the presence of PbO_2 was suggested. Finally, one peak for Pb_3O_4 (391 cm^{-1}) was visible and recurrent, but the absence of any other peaks made confirmation impossible. The analysis of the reddish deposits (F) revealed the presence of cerussite and/or hydrocerussite (peaks superposed), PbO, and PbO_2 (600 and 632 cm^{-1}).

As some doubts persisted with respect to the RAMAN results, complementary analyses using TOF-SIMS were carried out. A signal was difficult to obtain because of the high isolating power of lead oxides. The spectrum width analyzed could not include the hydrocerussite high atomic mass, and so hydrocerussite was reconstructed using oxide fragments. Species detected on A, B were: Pb, PbOH, PbO, $PbCO_3$, $(PbO)_2(H)_2$, Pb_3O_4, and PbO_2. Thus, the presence of hydrocerussite ($PbCO_3$þPbOH), PbO, Pb_3O_4, and PbO_2 was inferred. Cerussite was potentially present, but not validated. Low RAMAN detection of Pb_3O_4 and PbO_2 suggested that these species were present in trace amounts. On C and D, Pb, PbO, $PbCO_3$, and PbOH were detected. Only one spectrum presented PbO_2 at weak intensity. Thus, the presence of hydrocerussite, PbO and traces of PbO_2 were inferred.

To conclude, LSL deposits analysis revealed lead (II) oxides (carbonates, massicot/litharge) as predominant and traces of PbO_2 (Table 5).

Ten typical particles collected in the faucet aerator were analyzed with TOF-SIMS. Analysis did not reveal the presence of lead-based oxides (as found in LSL scale) on the particles, but many metals representative of PP (Sn, Cu, Zn) and iron were detected (Photo 1(bed)).

Table 4 e Linear regression analysis of particulate lead versus dissolved iron, and versus particulate iron, for each sample type.

x	y	Simple regression equation	R^2	p
Particulate Fe, 1L-RDT	Particulate Pb, 1L-RDT	y ¼ 1.2 þ 0.032x	0.34	<0.01
Particulate Fe, 2L-RDT	Particulate Pb, 2L-RDT	y ¼ 0.37 þ 0.093x	0.77	<0.01
Particulate Fe, 5min-RDT	Particulate Pb, 5min-RDT	y ¼ 0.21 þ 0.053x	0.68	<0.01
Dissolved Fe, 1L-RDT	Particulate Pb, 1L-RDT	y ¼ 0.65 þ 0.048x	0.22	<0.01
Dissolved Fe, 2L-RDT	Particulate Pb, 2L-RDT	y ¼ 0.029 þ 0.041x	0.49	<0.01
Dissolved Fe, 5min-RDT	Particulate Pb, 5min-RDT	y ¼ 0.025x	0.58	<0.01

4. Discussion

4.1. Relationship with metals from PP

Particulate lead, as opposed to dissolved lead, decreased significantly after flushing the 1st liter, and was not correlated with LSL length. Particulate lead in the 1st liter was correlated with particulate metals from PP and peak concentrations occurred simultaneously with particulate tin and/or particulate copper/zinc spikes. Establishing the source of the leaded particles is a challenge given that multiple sources of particulate lead can contribute sporadically and will produce different multi-metal signatures. Particulate lead at the tap has been weakly correlated with copper and zinc in samples collected using a wide range of sampling procedures and various PP materials (HDR Engineering Inc., 2009). Schock et al. (2008) investigated the composition of lead-based deposits in lead pipes and found moderate levels of copper, tin and zinc. Based on the simultaneous occurrence of particulate lead and other metals in the present study, a significant portion of the particulate lead measured in the 1st liter originates from the corrosion of lead-bearing materials in PP, namely by brass, solders and erosion of lead containing deposits. According to Sandvig et al. (2008), PP including faucets can contribute (21e38%) to the total lead mass measured at the tap from sequential samples collected at homes with LSLs. The simultaneous occurrence of zinc and lead is an indication of significant contribution of brass. In some homes, the sporadic spikes

of particulate lead occurring at the same time as Zn/Cu spikes could be due to brass dezincification, or to the presence of high leaded-brass (Grosvenor et al., 2005). Indeed, brass material from PP may contain lead up to the regulated level of 8% (LCR), or possibly more in older components (Lytle and Schock, 1996). Stagnation of water in faucets creates conditions favorable to corrosion that can lead to the detachment of particles of lead, zinc, or copper, or a combination of these elements (Dudi et al., 2005). In other homes, milder brass corrosion or the presence of low-leaded-brass could explain the lower levels of particulate lead, zinc, and copper. However, identifying the leading mechanism causing particulate lead release from brass is difficult in light of its sporadic release and the fact that different types of particles can be present at the same time. The simultaneous occurrence of lead and tin particles is a clear marker of solders. Tin occurred mainly in the particulate form, with
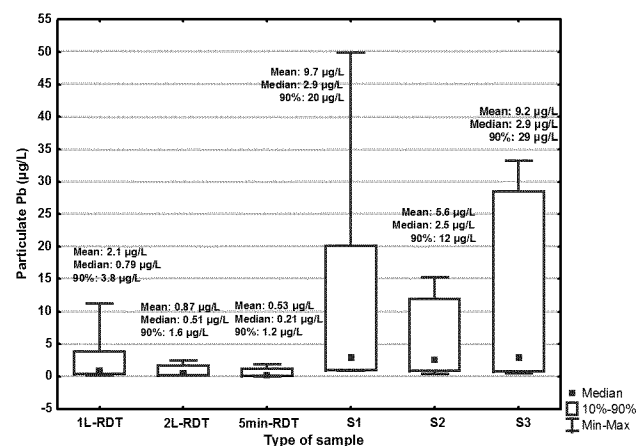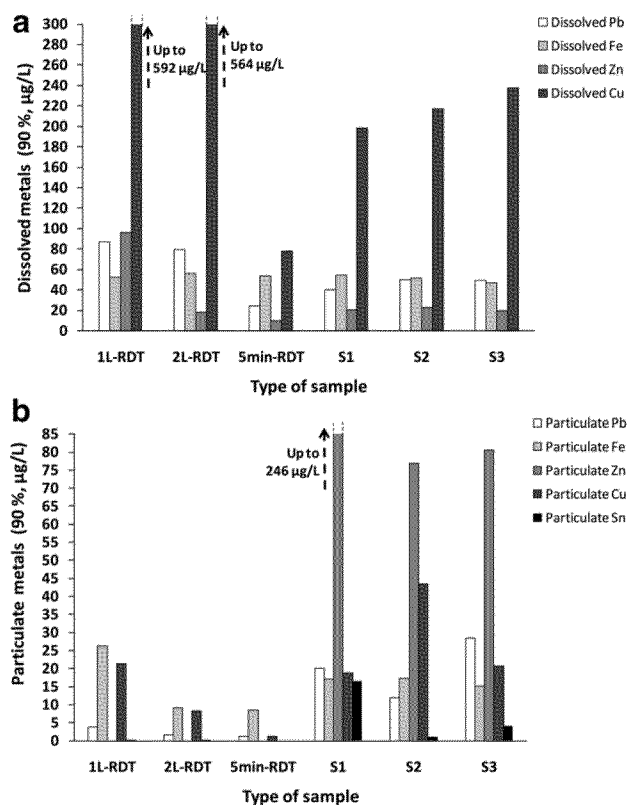
Fig. 5 e 90th Percentile of: (a) dissolved and (b) particulate metal concentrations measured at the tap for homes sampled with RDT D PSS sampling. N [9 for each bar.

Fig. 4 e Particulate Pb concentrations at the tap for homes sampled with RDT D PSS sampling. N [9 for each box.
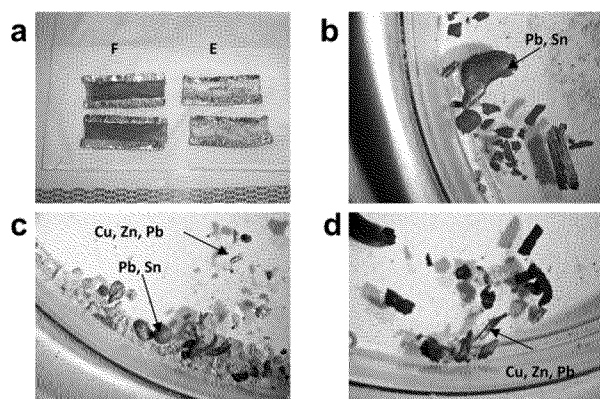
Photo 1 e (a) portions of lead service line E (right) and F (left); (b), (c), (d) examples of particles collected in the aerator tap after 2007 sampling.

concentrations measured either BDL (0.1 mg/L) or at relatively high levels (max RDT: 1.3 mg/L, max PSS: 33 mg/L) simultaneous to the highest concentrations of particulate lead. PbeSn solders joining copper piping have been shown to corrode and release particulate lead (Subramanian et al., 1995; Triantafyllidou et al., 2007). Particulate lead from solders was not as frequent as particulate lead from brass, and then only in the 1st liter.

Particulate lead decreased rapidly after the 1st liter sampled, and only weak correlations with PP metals remained. Consequently, for the system studied, flushing the 1st liter can eliminate most of the particulate lead originating from PP corrosion.

4.2. Relationship with particulate iron

Particulate lead in RDT samples was correlated with particulate iron. This correlation was even stronger in the 2 L-RDT and 5 min-RDT samples, and was accompanied by a correlation between particulate lead and dissolved lead. Strong correlations between lead particles/colloids at the tap and iron were also found in other studies (Hulsmann, 1990; HDR Engineering Inc., 2009). The observed correlation is most

likely the result of the sorption of dissolved lead from the LSL onto iron particles/deposits in LSL and PP, generating lead-loaded iron colloids and particles. Indeed, Schock et al. (2008) found major quantities of iron among other contaminants in lead-based internal deposits on lead pipes. Also, jar-tests conducted by HDR Engineering Inc. (2009) demonstrated that a lead-rich iron corrosion scale with variable lead levels (up to 7e8% Pb) could form via sorption mechanisms. Other studies show that iron scales in the distribution system can absorb and accumulate continuously low concentrations of many contaminants, such as arsenic. These scales can then release metals at hazardous levels in tap water following, for example, a change at the treatment plant (Reiber and Dostal, 2000; Lytle et al., 2004; Schock, 2005). Because of its affinity to iron scales, lead could accumulate in scales after years of exposure to low-lead levels in water, as observed for other metals such as arsenic in lead pipe scales (Schock et al., 2008). The presence and impact of leaded-iron scales should be considered if any treatment modifications leading up to water quality changes are scheduled because such changes could destabilize the scale or mobilize lead into solution, as observed for arsenic (Schock, 2005; Copeland et al, 2007). Except when the PP is galvanized-iron, iron originates from the corrosion of grey iron and unlined cast iron main pipes in the distribution network, and subsequent deposits of that iron in the LSL and PP (AWWARF and DVGW-TZW, 1996). In the present study, PP was investigated and galvanized-iron pipes were present in only one home. It is however possible that some inaccessible sections of the PP contained old galvanized-iron pipes potentially harboring lead-rich deposits. Also, iron scales could be present in copper piping due to the deposit of iron particles from the distribution main. These scales could generate sporadic release of lead-iron particles in RDT samples. The greater correlation with iron observed in the 2 L-RDT and 5 min-RDT samples is explained by the flushing of lead particles originating from the PP into the 1st liter. Actually, the correlation between particulate lead and dissolved lead increases with the presence of particulate iron as the PP and LSL are flushed. Iron-lead particles are considered to be the main contributor of particulate lead in the 2 L-RDT and the 5 min-RDT samples.

LSLs	Instrument	$PbCO_3$	$(PbCO_3)_2Pb(OH)_2$	PbO	Pb_3O_4	PbO_2	Conclusion
A, B	RAMAN (cm^{-1})	447, 668, 875, 900, 1055, 1808 1386 specific to $PbCO_3$		290, 427	N.D.	Weak intensity, characteristic peak absent	$PbCO_3$, $(PbCO_3)_2Pb(OH)_2$ PbO, traces of Pb_3O_4 and PbO_2
	TOF-SIMS	detected	detected	detected	detected	detected	
C, D	RAMAN (cm^{-1})	447, 668, 840, 900, 1055, 1808		343, 427	N.D.	Weak intensity, characteristic peak absent	$PbCO_3$ (maybe), $(PbCO_3)_2Pb(OH)_2$ PbO
	TOF-SIMS	detected	detected	detected	N.D.	Only one acquisition with little PbO_2 intensity	
E	RAMAN (cm^{-1})	447, 840, 1055, 1808		389, 427	391	387, 600, 607	$PbCO_3$ (maybe), $(PbCO_3)_2Pb(OH)_2$ PbO, traces of PbO_2
F		447, 900, 1055, 1367, 1808		290, 427	N.D.	600, 632	

Table 5 e Summary of oxides detected on LSLs with micro-RAMAN spectroscopy and TOF-SIMS.

Note: N.D. means not detected.

4.3.   Relationship with LSL

Analysis of the interior scale of 6 LSLs revealed the presence of a thin scale (w 40 mm) of lead (II) oxides, with only traces of tetravalent lead. The water quality in the distribution system studied is probably in the lead (II) formation zone of the Eh-pH diagram, but not far from the lead (IV) formation zone. Free chlorine residuals varied from 0.1 to 1.1 mg Cl_2/L, the higher range at some locations/periods possibly leading to the formation of patches of PbO_2 on lead (II) scale. Lead (IV) oxide has been mostly observed when high chlorine residuals were applied (Schock et al., 2001, 2005; Lytle and Schock, 2005). Our observations are consistent with the low to moderate chlorine residuals applied historically by this utility. Tetravalent lead is very stable, and detached particles exhibit low solubility (Edwards and Dudi, 2004). In contrast, lead carbonates are more soluble, but can still generate colloidal and particulate lead (McNeill and Edwards, 2004).

In this study, particulate lead was: (i) not correlated with LSL length, (ii) not significantly lower in "before 1970" homes, as compared to "wartime" homes with LSLs 2e3 times longer. This lack of correlation suggests that the detachment of lead oxides from LSLs is not a major source of particulate lead in this system. It is possible however that colloidal lead (0.1e0.45 mm) was present in our samples due to lead (II) scale detachment from LSL as observed by McNeill and Edwards (2004). Smaller colloids are included in the measurement of dissolved lead because of the 0.45 mm cutoff used.

The TOF-SIMS analysis of the particles collected in the aerators revealed the presence of elemental lead, but no traces of either lead (II) or lead (IV) oxides. However, several metals typically found in PP (Cu, Sn, Zn) and iron were detected simultaneously with lead. These findings support the conclusions of the statistical analyses, i.e. that particulate lead is the result of iron-lead scale detachment from PP/LSL and the local corrosion of lead-bearing materials in PP.

4.4.   Relationship with dissolved iron

The statistical analyses suggest that particulate lead increases with dissolved iron, particularly in the 2 L-RDT and 5 min-RDT samples. Iron release is related to the corrosion rate and constitutes a general indicator of the corrosivity of water (AWWARF and DVGW-TZW, 1996). Broo et al. (2001) proposed a model relating the corrosion rate in distribution systems to dissolved iron concentrations. If higher dissolved iron concentrations are indicative of greater water corrosivity, then greater corrosion of lead-bearing materials in PP and more frequent particulate lead detachment are expected. The impact of dissolved iron on particulate lead is more evident in the 2 L-RDT and 5 min-RDT samples, because most of the particulate metals originating from PP are flushed in the 1st liter.

4.5.   Influence of sampling parameters

Turbidity was found to be a significant factor determining particulate lead concentrations in the 1 L-RDT samples. As particulate lead in these samples was correlated with concentrations of particulate metals from PP and iron, all these metals may contribute directly to turbidity.

The incidence of particulate lead at the tap can originate from the removal of existing deposits by scouring or sloughing during water flow (Schock, 1990). In this study, the passage of particulate lead (including lead-iron particles) was influenced in 2 L-RDT, and 5 min-RDT samples by flow rate. Indeed, particulate lead spikes of 2.5, 2.4 mg/L (2 L-RDT) and 4.5, 1.8 mg/L (5 min-RDT) were recorded at the two highest flow rates (12 and 8.7 L/min, i.e. w1.1e1.6 m/s for a 0.5 in. diameter pipe). However, a higher particulate lead release event was recorded at a lower flow rate of 7.5 L/min, i.e. w1 m/s for a 0.5 in. diameter pipe (2 L-RDT: 7.4 mg/L, 5 min-RDT: 3.5 mg/L). This is consistent with results for small iron oxide particles (45e250 mm) suspended at a velocity >0.13 m/s, and fully suspended at a velocity >0.22 m/s. Large particles grouped into "islands" required a 0.4 m/s velocity (Slaats et al., 2003). The impact of flow rate on the presence of a particle at the tap depends on particle characteristics, piping configuration defining the flow regime, and the distance of detached particles to the tap. It is therefore expected that the relationship between flow rate and particulate lead at the tap would be site-specific and more difficult to establish in many homes with particles of varying size and density. Moreover, recent pipe loop testing has shown that lead particles released from galvanized-iron pipes were sensitive to modifications in flow regime, but that the level of sensitivity was really variable between the pipes tested (HDR Engineering Inc., 2009).

In the present study, flow rates ranged from 3.0e7.5 L/min (76% of homes sampled), very low and very high flow rates being less common (1e2.5 L/min: 11%; >7.5 L/min: 13%). Systematic tap sampling at increasing flow rates may provide a clearer picture. In a high-risk home in Washington D.C., increasing the flow rate from 1 to 22 L/min resulted in a dramatic increase in particulate lead (Triantafyllidou and Edwards, 2009). However, similar tests conducted in our system at flow rates between 4.6 and 15 L/min showed no increase in dissolved and particulate lead at the tap (Nour et al., 2007). Finally, flow rate did not influence particulate lead in the 1st liter, because particulate lead in these samples reflects an accumulation of particulate metals during stagnation.

4.6.   Importance of the sampling protocol

The importance of the sampling protocol can be evaluated by comparing particulate lead in the 1st liter collected with the 2007-RDT and 2006e30MS sampling protocols. Overall, a greater proportion (30%) of samples collected with RDT sampling (45 homes) contained more than 1 mg/L of particulate lead when compared to 11% for the 30MS sampling (109 homes). Moreover, the 90th percentile value for the 1 L-RDT samples exceeded the value for the 1 L-30MS samples by 57% (Fig. 1b). When using the 30MS sampling, the 5 min flushing prior to stagnation is often performed at maximum flow rate, which is likely to eliminate most particles. The subsequent stagnation of 30 min may not be long enough to regenerate particles. The RDT sampling appears to be a better approach of estimating particulate lead at the tap, because: (i) particles are not systematically flushed out of the system shortly before sampling; (ii) prior usage patterns vary and may have been favorable to particle flow transport to the tap. Moreover, RDT sampling is considered to provide a better range of typical

consumer exposure, provided that sufficient samples are taken (van den Hoven and Slaats, 2006; Cardew, 2009). However, it is possible that RDT sampling would reveal less particulate lead than the reference LCR sampling (~ 6 h stagnation). A possible approach to obtaining pertinent information on both particulate and dissolved lead would be to sample the 1st liter upon arrival for particulate lead analysis (RDT), and then to flush and analyze the 30MS samples for dissolved lead.

After 5 min of flushing, hydraulic disturbances caused by PSS increased the passage of particulate metals, including particulate lead, into the tap water to levels higher than those found in the 1 L-RDT samples. Indeed, the particulate lead to total lead ratio increased from 2% in the RDT samples to 33% (90th percentile) in the PSS samples. Increases were higher for particulate metals from PP (Cu, Zn, Sn). These observations support the conclusions that particulate lead originates partly from brass element/solder corrosion and increases with flow rate. The repeated activation (5 times) of the faucet at high flow rate created hydraulic disturbances and friction that have been shown to impact particulate lead release (van den Hoven and Slaats, 2006). Also, hydraulic disturbances such as water hammer were shown to increase particulate lead detachment from lead-iron scales in galvanized-iron piping (HDR Engineering Inc., 2009). Water quality determines corrosivity, and combined with hydraulic and physical conditions, determines the formation and release of particulate lead. However, the detection of particles is a function of particle transport to the tap and passage through the aerator (if present). The conditions of particle accumulation and transport vary depending on the flow rate and prior flushing. In this system, the selection of the sampling protocol would directly influence compliance, as particulate lead may contribute to more than action levels when using PSS.

Additionally, PSS increased dissolved metals, especially lead, copper, and zinc. PSS samples were collected immediately after the 5 min-RDT sample without any stagnation providing time for the dissolution of lead. It is consequently inferred that the higher dissolved lead content with the PSS (versus RDT) is due to colloidal lead detachment, either from LSL or PP. This raises issues regarding the definition of dissolved lead as the fraction <0.45mm. Dissolved lead measured in this way may include a significant colloidal fraction that behaves as particulate lead and is sensitive to flow rate and hydraulic disturbances.

5.   Conclusions

This study provides an analysis of the source, occurrence, and parameters affecting the release of particulate lead. Particulate lead, for the system investigated, was attributed to PP corrosion and leaded-iron scale detachment. Results show that current sampling protocols are not adapted for the detection of particulate lead and may underestimate a part of the consumer exposure at the tap. Consumers' usage patterns and high flow rates can stimulate the detachment of lead particles and should be considered in sampling protocols. The strong relationship observed between iron and particulate lead raises concerns about the potential accumulation and subsequent release from scales in PP, especially in the presence of galvanized-iron. Also, the traditional definition of particulate lead might be revised to account for the colloidal detachment observed during PSS. Finally, efforts to measure particulate lead are justified by the sporadic but sometimes extreme concentrations that can occur and their potential impact on health.

r e f e r e n c e s

AWWARF (AWWA Research Foundation) and DVGW-TZW (Technologiezentrum Wasser), 1996. In: Internal Corrosion of Water Distribution Systems, second ed. Colorado, Denver.

Broo, A.E., Berghult, B., Hedberg, T., 2001. Drinking water distribution: improvements of the surface complexation model for iron corrosion. Water Science and Technology: Water Supply 1 (3), 11e18.

Cardew, P.T., 2009. Measuring the benefit of orthophosphate treatment on lead in drinking water. Journal of Water and Health 7 (1), 123e131.

Cartier, C., Laroche, L., Deshommes, E., Nour, S., Prévost, M., 2008. Impact of Sampling Mode, Water Chemistry and Pipe Characteristics on Lead Dissolution at the Tap. CWWA, Quebec City.

Copeland, R.C., Lytle, D.A., Dionysiou, D.D., 2007. Desorption of arsenic from distribution system solids. Environmental Monitoring and Assessment 127 (1e3), 523e535.

Dudi, A., Schock, M., Murray, N., Edwards, M., 2005. Lead leaching from inline brass devices: a critical evaluation of the existing standard. Journal of the American Water Works Association 97 (8), 66e78.

Edwards, M., Dudi, A., 2004. Role of chlorine and chloramine in corrosion of lead-bearing plumbing materials. Journal of the American Water Works Association 96 (10), 69e81.

Edwards, M., Triantafyllidou, S., Best, D., 2009. Elevated blood lead levels in young children due to lead-contaminated drinking water: Washington, DC, 2001e2004. Environmental Science and Technology 43 (5), 1618e1623.

Giani, R., Keefer, W., Donnelly, M., 2005. Studying the Effectiveness and Stability of Orthophosphate on Washington DC's. AWWA-WQTC, Quebec City, Quebec.

Safe drinking water act, 2002, Ontario Regulation 243/07 Schools, Private Schools and Days Nurseries, 2002. Government of Ontario, Ontario.

Grosvenor, A.P., Martin, R.R.H., Giuliacci, M., Biesinger, M.C., 2005. Evaluation of multiple analytical techniques in the study of leaching from brass fixtures. Canadian Journal of Analytical Sciences and Spectroscopy 50 (2), 97e107.

Gump, B.B., Stewart, P., Reihman, J., Lonky, E., Darvill, T., Parsons, P.J., Granger, D.A., 2008. Low-level prenatal and postnatal blood lead exposure and adrenocortical responses to acute stress in children. Environmental Health Perspectives 116 (2), 249e255.

HDR Engineering, Inc., 2009. An Analysis of the Correlation Between Lead Released from Galvanized Iron Piping and the Contents of Lead in Drinking Water. District of Columbia

Water and Sewer Authority (DCWASA), Bellevue, Washington.

Health Canada, 2009. Guidance on Controlling Corrosion in Drinking Water Distribution Systems. Federal-Provincial-Territorial Committee on Drinking Water and Federal-Provincial-Territorial Committee on Health and the Environment, Ottawa, Ontario.

van den Hoven, T., Slaats, N., 2006 (Chapter 3). In: Quevaullier, P., Thompson, K.C. (Eds.), Lead Monitoring. Wiley and Sons, Inc.

Hulsmann, A.D., 1990. Particulate lead in water-supplies. Journal of the Institution of Water and Environment Management 4 (1), 19e25.

Jusko, T.A., Henderson Jr., C.R., Lanphear, B.P., Cory-Slechta, D.A., Parsons, P.J., Canfield, R.L., 2008. Blood lead concentrations <10 microg/dL and child intelligence at 6 years of age. Environmental Health Perspectives 116 (2), 243e248.

Lanphear, B.P., Burgoon, D.A., Rust, S.W., Eberly, S., Galke, W., 1998. Environmental exposures to lead and urban children's blood lead levels. Environmental Research 76 (2), 120e130.

Lanphear, B.P., Dietrich, K., Auinger, P., Cox, C., 2000. Cognitive deficits associated with blood lead concentrations <10 microg/dL in US children and adolescents. Public Health Reports 115 (6), 521e529.

Lanphear, B.P., Hornung, R., Ho, M., Howard, C.R., Eberly, S., Knauf, K., 2002. Environmental lead exposure during early childhood. The Journal of Pediatrics 140 (1), 40e47.

Lytle, D.A., Schock, M.R., 1996. Stagnation Time, Composition, pH, and Orthophosphate Effects on Metal Leaching from Brass. United States Environmental Protection Agency (USEPA), National Risk Management Research Laboratory, Office of Research and Development, Washington, D.C.

Lytle, D.A., Sorg, T.J., Frietch, C., 2004. Accumulation of arsenic in drinking water distribution systems. Environmental Science and Technology 38 (20), 5365e5372.

Lytle, D.A., Schock, M.R., 2005. Formation of Pb(IV) oxides in chlorinated water. Journal of the American Water Works Association 97 (11), 102e114.

McNeill, L.S., Edwards, M., 2004. Importance of Pb and Cu particulate species for corrosion control. Journal of Environmental Engineering 130 (2), 136e144.

Nour, S., Prévost, M., Cartier, C., Laroche, L., Edwards, M., 2007. Impact of Sampling Flow Rate, Flushing, and Faucet Aerator on Dissolved and Particulate Lead Concentrations at Consumer Tap. AWWA-WQTC, Charlotte, North Carolina.

Reiber, S., Dostal, G., 2000. Well water disinfection sparks surprises. Opflow 26 (3), 5.

Sandvig, A., Kwan, P., Kirmeyer, G., Maynard, B., Mast, D., Rhodes Trussell, R., Trussell, S., Cantor, A., Prescott, A., 2008. Contribution of Service Line and Plumbing Fixtures to Lead and Copper Rule Compliance Issues. AWWARF, Denver, Colorado.

Schock, M.R., 1990. Causes of temporal variability of lead in domestic plumbing systems. Environmental Monitoring and Assessment 15 (1), 59e82.

Schock, M.R., Harmon, S.M., Swertfeger, J., Lohmann, R., 2001. Tetravalent Lead: A Hitherto Unrecognized Control of Tap Water Lead Contamination. AWWA-WQTC, Nashville, Tennessee.

Schock, M.R., Scheckel, K., DeSantis, M., Gerke, T., 2005. Mode of Occurrence, Treatment, and Monitoring Significance of Tetravalent Lead. AWWA-WQTC, Quebec City, Quebec.

Schock, M.R., 2005. Distribution Systems as Reservoirs and Reactors for Inorganic Contaminants, Ch. 6 in Distribution System Water Quality Challenges in the 21st Century. AWWA, Denver, Colorado, pp. 105e140.

Schock, M.R., Hyland, R.N., Welch, M.M., 2008. Occurrence of contaminant accumulation in lead pipe scales from domestic drinking-water distribution systems. Environmental Science and Technology 42 (12), 4285e4291.

Slaats, L.P.M., Rosenthal, W.G., Siegers, M., van den Boomen, M., Bueken, R.H.S., Vreeburg, J.H.G., 2003. Processes Involved in The Generation of Discolored Water. AWWARF and Kiwa Water Research, Denver, Colorado.

Subramanian, K.S., Sastri, V.S., Elboujdaini, M., Connor, J.W., Davey, A.B.C., 1995. Water contamination: impact of tin-lead solder. Water Research 29 (8), 1827e1836.

Triantafyllidou, S., Parks, J., Edwards, M., 2007. Lead particles in potable water. Journal of the American Water Works Association 99 (6), 107e117.

Triantafyllidou, S., Edwards, M., 2009. Lead (Pb) in U.S. drinking water: school case studies, detection challenges and public health considerations. Yale University Drinking Symposium on Your Solution for the 21st Century, New Haven, Connecticut.